

**KABARAK**



**UNIVERSITY**

**UNIVERSITY EXAMINATIONS**  
**2009/2010 ACADEMIC YEAR**  
**FOR THE DEGREE OF BACHELOR OF SCIENCE IN**  
**EDUCATION SCIENCE**

**COURSE CODE: CHEM 322**

**COURSE TITLE: METHODS OF STRUCTURAL  
DETERMINATION**

**STREAM: SESSION VII & IX**

**DAY: TUESDAY**

**TIME: 2.00 – 4.00 P.M.**

**DATE: 01/12/2009**

---

**INSTRUCTIONS:**

**Attempt all questions:**

**Total Marks 70 (Each 17.5 marks)**

**PLEASE TURN OVER**

1. (a) (i) Distinguish between bathochromic shift and hypsochromic shift as used in UV-Visible spectroscopy? Give examples. (3 mks)
- (ii) Distinguish between hyperchromic effect and hypochromic effect as used in UV-Visible spectroscopy? Give examples. (3 mks)
- (b) The following compounds were irradiated with UV radiation: chloroethane, propanone, 2-butenal and cyanopropane.
- (i) Identify all possible transitions that will occur in each molecule. (3 mks)
- (ii) Arrange the transitions according to increase in energy. (2.5 mks)
- (c) (i) The UV spectrum of 3-buten-2-one in hexane shows absorption maximum at 226 nm in hexane solution. Predict which direction the absorption maximum would shift if the solvent is changed to ethanol? (3 mks)
- (ii) Explain why ethanal absorb UV radiation at wavelength of 293 nm and propanone absorbs at a wavelength of 279 nm? (3 mks)

2. (a) (i) Explain the different absorption trends observed in bond stretching of the following bonds: (3 mks)

	C-H	C-C	C-O	C-Cl
Frequency in $\text{cm}^{-1}$	3000	1200	1100	800

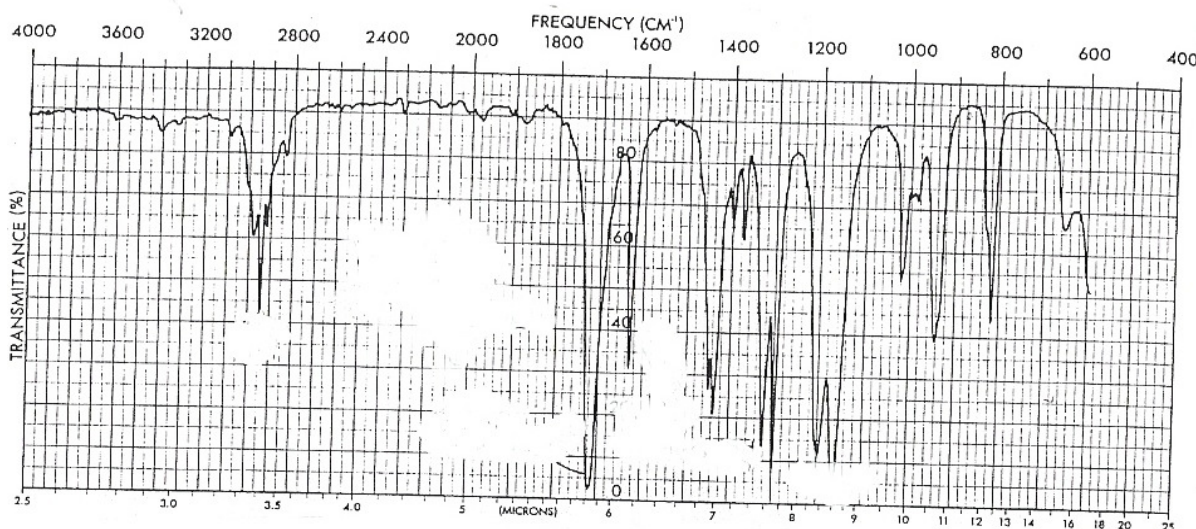
- (ii) Normal ketone has its C=O stretch vibration at  $1715 \text{ cm}^{-1}$  while a conjugated one has its frequency between  $1675\text{-}1680 \text{ cm}^{-1}$ . Explain (3 mks)
- (b) (i) Explain the difference in the frequencies of IR – absorption in C-H bond stretch of the following compounds. (3 mks)

	Alkane	Alkene	Alkyne
	C-H	=C-H	$\equiv\text{C-H}$
Frequencies $\text{cm}^{-1}$	2900	3100	3300

(ii) Explain the difference in the frequencies of IR – absorption in carbon-carbon stretch of the following compounds. (3 mks)

	Alkene	Alkyne
	C=C	C≡C
Frequencies $\text{cm}^{-1}$	1650	2200

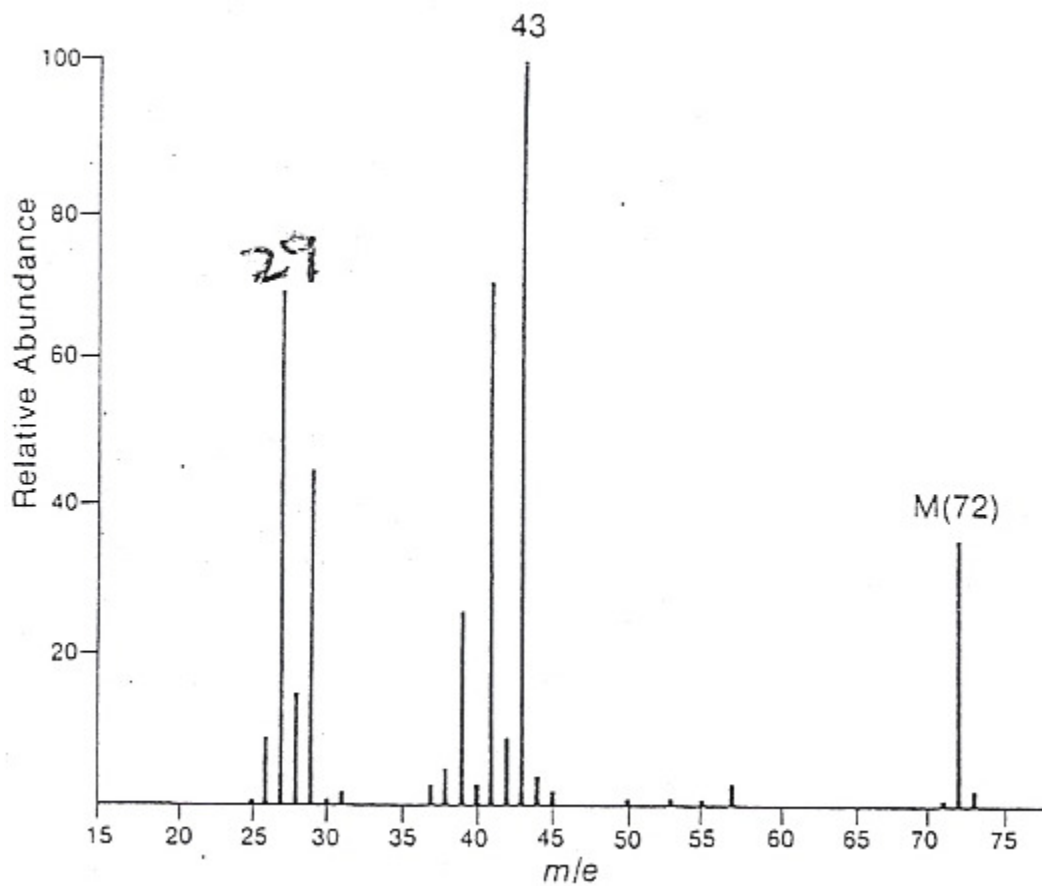
(c) The IR spectrum below is for a molecule with general formula  $\text{C}_5\text{H}_7\text{O}_2$ . Identify all the functional groups present in the molecule and give the corresponding vibrational frequencies. (5 mks)



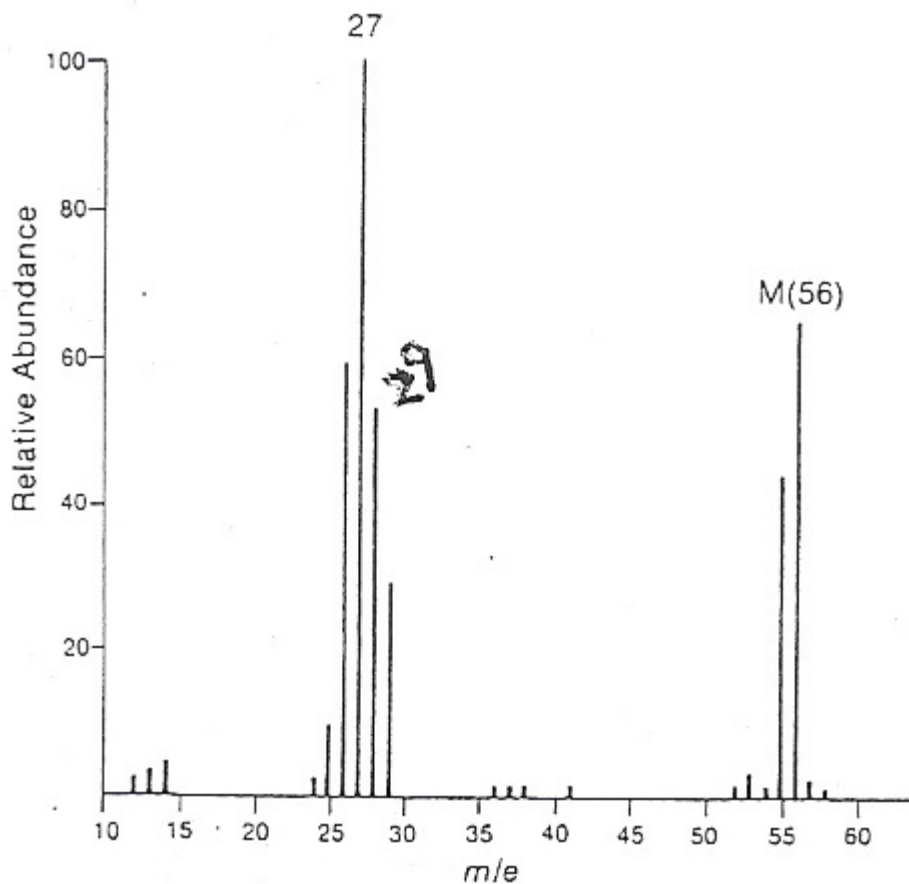
3. (a) Describe with aid of a schematic diagram the principle behind mass spectroscopy as a technique for analysis. (6 mks)
- (b) (i) Give all possible fragmentation units of isopropyl benzene that are formed when subjected to mass spectroscopic analysis. (3.5 mks)
- (ii) Explain why a strong peak at  $m/e$  105 is observed in the mass spectrum of isopropyl benzene. (2 mks)
- (c) Use the mass spectra below (i) to identify the compound between 2-methylpropanal and 2-propenal that corresponds to each spectrum. (3 mks)

Assign the fragmentation units for each molecule in question 2 (c) (i) above to their corresponding mass-charge ratio peaks. (3 mks)

### Spectrum A

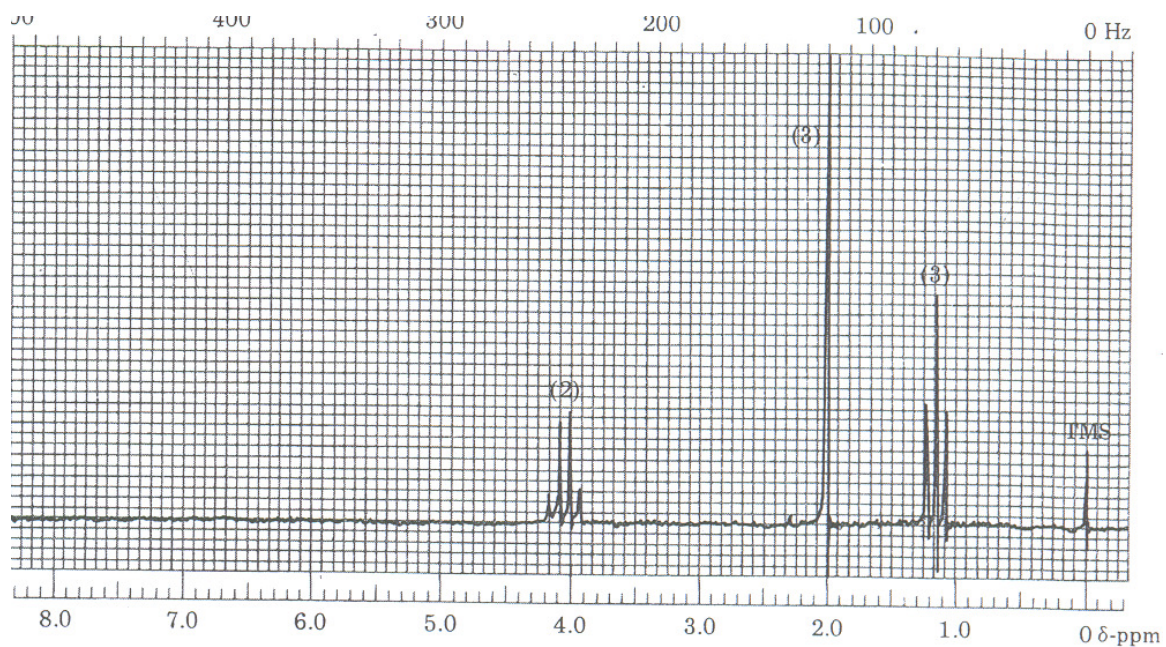


### Spectrum B



- 4) (a) Give a flow chart of NMR-spectrometer and explain the functions of magnetic field and radiowave radiation in analysis. (5 mks)
- (b) (i) Explain how chemical shift of a proton is affected by electronegativity of an heteroatom adjacent to the proton. (2 mks)
- (ii) In benzaldehyde two of the ring protons have resonance at  $\delta = 7.72$  and the other three protons have resonance at  $\delta = 7.40$ . Draw the structure of benzaldehyde and assign the resonance to the corresponding protons. (2 mks)
- (iii) Explain the difference in the resonance of the protons in (b) (ii). (2 mks)

(c) The NMR spectrum below is from spectral analysis of an ester with general formula  $C_4H_8O_2$  (6.5 mks)



Give the structure of the ester and assign the chemical shift values to the protons giving rise to the peaks.